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Use of Manganese Salts in the Separation and Determination of Phosphoric Acid

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THE USE OF MANGANESE SALTS

IN THE

SEPARATION AND DETERMINATION OF PHOSPHORIC ACID

BY

HARRY HASSON

THESIS

FOR THE DEGREE OF

BACHELOR OF SCIENCE IN CHEMISTRY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Harry Hasson

ENTITLED The Use of Manganese Salts in the Separation & Determination of Phosphoric Acid

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science in Chemistry

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The determination of phosphoric acid has become of prime importance during the last fifty years. The accurate estimation of phosphates in fertilizing materials and of phosphorus in iron and steel has caused a great demand for a convenient and accurate method. Consequently much work has been done along this line and numerous methods, valuable and otherwise have been proposed and more or less used by various chemists. As the object of the method proposed in this thesis is chiefly the determination of the phosphates contained in fertilizers, the discussion will be confined to that phase of the subject.

To get a better view of the investigations that have been carried out it may be well to divide the methods into two classes, namely; gravimetric and volumetric. No attempt

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will be made to enumerate all of the methods which have been proposed in the past, but a few of the most important ones, which have at some time been used in actual practice, will be briefly considered, in order to get an insight into their best points and some idea as to their comparative value. In the course of so many investigations it is almost impossible that many worthless methods should not have been published and it is necessary to compare a proposed method with the best processes known before its real value can be determined.

By far the most important of the gravimetric methods are those which depend upon the precipitation of the phosphoric acid as the ammonium-magnesium phosphate and the subsequent burning of this salt

to magnesium pyrophosphate. The difficulty in this precipitation lies in the fact that it must take place in strongly ammoniacal solution. Such a condition is favorable to the precipitation of the phosphates of the earth and alkaline earth metals. Not only the phosphates, but also hydroxides or other salts may come down under these conditions. To overcome this, two different means are employed, namely:- 1. the addition of salts to the solution so that all of these other substances may remain dissolved, while the ammonium magnesium phosphate alone is precipitated; 2. the precipitation of the phosphoric acid as ammonium phospho-molybdate from the nitric acid solution of the phosphates, whereby all of these interfering materials are retained in solution. This precipitate is then dissolved and the phosphoric acid

precipitated as ammonium-magnesium phosphate.

In the first method,* [42] the salts added are such as ammonium citrate, ammonium tartrate, etc. These are dissolved in the solution of phosphoric acid to be analyzed. Then the liquid is made ammoniacal and magnesia mixture is added. The ammonium citrate is now used nearly altogether for this purpose. This method has been closely studied by Fresenius, who determined its weak points, viz:- 1. if any silica has been dissolved in the solution of the original substance it will be precipitated when the excess of ammonia is added; 2. the ammonium-magnesium phosphate is slightly soluble in a solution of ammonium citrate. These objections are not so noticeable in actual work as might be supposed, and in fact tend to counterbalance one another. The method is still

* The numbers refer to the Bibliography

used in commercial work where time is a great factor and great accuracy is not so much sought after.

The second method[1,2,3,4,5&6] enumerated depends (1) upon the insolubility of ammonium phospho-molybdate in dilute nitric acid, (2) upon the complete precipitation of this salt upon the addition of a nitric acid solution of ammonium molybdate to a solution of a phosphate. The yellow molybdate precipitate is easily soluble in ammonium hydroxide and after being dissolved is determined by adding magnesia mixture in the usual way. One defect of this method is that in the precipitation of the phospho-molybdate care must be taken that the solution is not heated above 85°-90° C. as the ammonium molybdate will decompose and some molybdic oxide will be thrown down. This is difficultly soluble in ammon-

ium hydroxide and consequently may contaminate the ammonium-magnesium phosphate precipitate and thus vitiate the results. It is generally conceded that this is the most accurate method we have for phosphoric acid determination. It is the one officially adopted and in use by the Association of Official Agricultural Chemists of the United States. The great objection is to the two precipitations and to the time which the process takes.

A modification[7,+9] of this method has lately been worked out; the weighing of the yellow precipitate. When the method was first proposed it was considered that the precipitate was of indefinite composition but later experimenters claim that the conditions can be so regulated as to obtain a uniform compound. Hladding has investigated the subject and finds that the chief difficulties

or rather causes of error have been the temperature of precipitation and temperature of drying the yellow precipitate. By adding the molybdate solution slowly he prevents the occlusion of salts by the precipitate. The presence of a large amount of ammonium nitrate in the solution insures a complete precipitation. A low temperature (50° C) prevents the separation of molybdic oxide or iron salt. He dries the salt on the filter paper at 105° C. For this purpose he uses a glycerol oven to keep the temperature constant. He obtained results which agreed perfectly with the magnesium precipitation of the yellow precipitate.

Many other gravimetric methods have been proposed but most of them are not useful in the presence of Fe and Al. Without going into details, the precipitations as lead, tin and bismuth phos-

phates may be mentioned.[2] Also the uranic phosphate method.[10-11] This latter has given very good results and may be used in the presence of iron and aluminum by using ammonium citrate in the solution.

The volumetric processes are based primarily upon the gravimetric ones. They may be divided into three classes: (1) Precipitation methods, (2) Oxidimetric methods, (3) Alkalimetric methods. To the first division belongs the determination by means of uranium.[1-5, 12-17] This method is based on the fact that if a solution of uranium acetate or nitrate be added to a solution of phosphate slightly acidulated with acetic acid, uranic phosphate is precipitated. The end reaction is determined by means of the deep brown color given by uranium salts when they come in contact with potassium ferrocyanide. The slightest excess of uranium in the solution

may be shown by means of spot tests with the ferrocyanide. This method is described by Sutton,[15] who claims to have devised it. Neubauer and Pincus also published the same method, but independently of each other and Sutton. The method has been fully investigated by various chemists. Many points have to be observed to obtain strictly accurate results. Ammonium salts, particularly the acetate, have an effect upon the end reaction, and if their presence is unavoidable, they must always be present in the same amounts. The method is inapplicable in the presence of iron and aluminium salts. This latter difficulty may be gotten around by previous precipitation of the phosphoric acid as ammonium-magnesium phosphate. The amount of alkaline acetate, (i.e. sodium acetate) must always be the same in each titration.

The liquid must be warm and yet if heated too hot calcium phosphate will precipitate. To avoid this Fresenius proposed an inversion of this method, that is, titration with the phosphate solution into a given quantity of standard uranium solution. Most of those who have used this inverted method claim that it is not necessary and is a waste of time. The uranium titration has been much used, especially in Germany, and was for a number of years official at some of the experiment stations there, notably the one at Halle.

Pemberton[18] has proposed a method for the use of the molybdic precipitation volumetrically. He adds the ammonium molybdate solution to the solution of phosphate until no more of the yellow molybdate is thrown down. This is determined by a

specially devised test filter, by which a small quantity of the liquid may be filtered and tested with molybdate. This method has not been much employed.

The volumetric method[19,20,21] which seems to have given the best results and promises most is the titration of the yellow precipitate with potassium permanganate. This comes under the division of oxidimetric methods. It depends upon the reduction of the solution of the yellow precipitate by hydrogen. This is accomplished by dissolving in ammonium hydroxide. Then dilute sulphuric acid is added to slight acidity. The solution is then run through a Jones reductor and titrated with standard permanganate. The solution is reduced from the molybdic to the molybdous form, (from MoO_3 to Mo_2O_3). Blair[21] gives the reduction as from MoO_3 to $Mo_{24}O_{37}$. If the reduction is carried

out in a closed flask instead of in the reductor, in order to avoid the reoxidation of the air, the final product is Mo_2O_3 according to Blair. This method has been much used for determining the phosphorus in steels but it was not until 1896 that its use was adapted to fertilizer work by Maxwell.

Of the alkalimetric methods that of Pemberton[6,18] is the most employed and most important. His method is based on the fact that if the yellow precipitate is titrated with alkali, with phenol-phthalein as indicator, one molecule of P_2O_5 represents twenty three molecules of sodium hydroxide. The quantity of P_2O_5 should consequently be small and the chance for error is great. The method requires much experience to obtain accurate results. Nevertheless it has been adopted as a volumetric method by the Association of Official Agri-

cultural Chemists after careful trial.

Many comparative tests have been made of these methods, notably by Schumann[4,5]; Kissel[3]; Fresenius[2]; Neubauer, & Luck; Abesser; Jani, and Märcker. These investigators have proven the superiority of the molybdate gravimetric determination, with the final weighing as magnesium pyrophosphate, over all other gravimetric methods and have given the conditions under which it can be most conveniently operated. Improvements have been made subsequently and we may accept the official method of the Association of Official Agricultural Chemists as the most accurate of all methods for the determination of phosphoric acid. As to volumetric methods, the German investigators have established the accuracy of the uranium ~~titration~~ but it is not applicable in all cases. The Pemberton alkalimetric method is

worthy of consideration, as it has been adopted by the A. O. A. C. only after careful investigation. The permanganate titration of the yellow precipitate as used in iron and steel work has been put to a severe test and is in general use in this line. It has not been much used for fertilizer analysis however. Maxwell, in 1896 showed its applicability to this work and its superiority over the methods now in use. In a number of determinations by him the percentage did not vary one tenth of a per cent from that obtained by the gravimetric method. The method deserves more attention and a more general trial.

In this thesis the attempt has been made to utilize the tribasic phosphate of manganese in the determination of phosphoric acid volumetrically. The process as first conceived is as follows: Manganese

salt is added in excess to the phosphoric acid solution. The solution is now boiled and made neutral to litmus with ammonia. This precipitate supposedly tri manganese phosphate, after having been washed, is dissolved in hydrochloric acid and the manganese precipitated with hydrogen peroxide. This precipitate of oxide of manganese is titrated by means of ammonium sulphocyanate and potassium permanganate in the presence of dilute sulphuric acid. This then would fall under the second division of volumetric methods as it is an oxidation process. In addition to the investigation of this determination it was desired to test the efficiency of the manganese salts in the removal of the phosphates previous to the analysis of the alkalis in water. In the course of the experimenting this assumed a minor place and the attention was directed more partic-

ularly to the analytical method. The nature of this method naturally divided the work into two parts, namely: (1) the investigations on the manganese phosphate precipitate, (2) those on the determination of the manganese in this precipitate. These two phases of the subject will be considered in the order named.

Not much work has been done on the trimanganese phosphate. Practically no investigations have been carried out during the last twenty years. The following references will give some idea as to the extent of the literature on this branch of the subject.

In 1848 Heintz[220] made a study of the manganese phosphates. His work was mostly confined to methods of production. He prepared the trimanganous phosphate by adding sodium phosphate to a solution of manganese sulphate. The precipitate obtained was white

and uncrystallized, almost insoluble in water, soluble in acids.

In 1861, Debray[23] conducted a series of investigations on the method of production of a number of phosphates and among these was the trimanganophosphate. He found that if a solution of phosphoric acid and manganese carbonate are heated to 70°C., the di-manganous-salt is obtained. If these crystals are heated in water to 100°C. the trimanganophosphate separates out and leaves some lower phosphate of manganese in solution. If manganese is in excess, the phosphoric acid is precipitated in the form of the crystallized tribasic phosphate, if boiling is continued. He also proved that no chloro-phosphate was formed by use of manganese chloride instead of carbonate. This shows a behaviour at variance with that of calcium and lead.

In 1877, Erlenmeyer[24] and Heinrich carried out a series of experiments

on the phosphates of manganese. They found that the tribasic salt is formed if the sulphate of manganese is treated with disodium hydrogen phosphate. They did not find it to be formed by heating the dimanganic salt with water as Reveray had stated. They found that on treating the dimanganophosphate with cold water, a crystallized, tri-manganophosphate was formed.

In 1868, Braun[25] published some of the following facts:- If one adds a solution of manganese chloride to a solution of disodium hydrogen phosphate a white precipitate is formed. If one adds microcosmic salt to a solution of manganese chloride with the manganese in excess and heats to boiling, the white precipitate, which at first is flocculent will become crystalline and in such state forms the tribasic phosphate with seven equivalents of water. If one adds the manganese chloride to the microcosmic salt with the latter in excess,

the silky crystalline precipitate of manganese ammonium phosphate is formed.

In 1887, Joly[26] published a series of articles on the earthy phosphates, principally concerning their heats of formation, but containing several facts which may be applied to the precipitate in the method to be described. He found that there were two distinct stages in the precipitation of the earthy phosphates, first, a colloidal state and then a crystalline state. The heat of formation of this second was considerably greater than the first. If alone, the colloidal salt is transformed into the crystalline form without any further change. If, however, the colloidal precipitate is in the presence of some alkaline chloride, sodium chloride for example, a new phenomena occurs; the first salt changes more or less slowly into a double crystallized salt, containing two equivalents of the earthy

metal to one of the alkali. He also states that the first precipitate may enclose a certain quantity of double gelatinous phosphate, which on crystallizing determines the transformation of the whole mass.

In 1887, Berthelot[27] published a paper on phosphates and brought up the same points as Joly. He speaks of the colloidal and crystalline states of the tribasic phosphates of the earthy metals and of the decomposition in presence of an alkaline chloride with the formation of a double salt.

It will be seen by these references that most of the literature on the subject of the trimanganophosphate is confined to its method of preparation. Deveray's statement that no chloro-phosphate is formed by heating the salt with an excess of manganese chloride; Braun's statement in regard to the formation of the salt in an excess of manganese; Joly's mention

of the colloidal state of the precipitate, and the subsequent transformation of this into the crystalline form. As well as his statement in regard to the formation of double salts; all have a direct bearing on the precipitation of the trimanganophosphate.

Special reference will be made here to the work of Lindeman and Motten[28] (1895), because of the similarity of their investigations to those which have been carried out in this thesis. Their method consists in the precipitation of the phosphoric acid in the state of ammonium-manganese phosphate and the determination of the manganese in this volumetrically by the precipitation with H_2O_2 to the higher oxide and the titration of this oxide iodometrically. In their method the solution containing the phosphoric acid is made up to the same volume every

time. To this are added (the quantities of reagents being closely adhered to), 10 c.c. of ammonium hydroxide, 25 c.c. of a solution of ammonium citrate, 25 c.c. of a manganese sulphate solution (2.5%), 10 c.c. ammonium chloride (20%). The mixture takes on a brownish color, changing to yellowish on boiling and finally decolorizing. While the liquid boils it is stirred with a glass rod and the precipitate of ammonium manganese phosphate comes down as silky, pale rose colored crystals. A few minutes of boiling are sufficient. The mixture is cooled, filtered, and the precipitate washed with 100 c.c. ammonium chloride solution (.5%). The filtration and washing of the precipitate should be carried out as quickly as possible and should take only a very few minutes. The precipitate is redissolved in dilute hydrochloric acid and returned to the beaker in which the precipitation was made. It is then

diluted to 200 - 300 c.c. with water and the precipitation made with hydrogen peroxide. (see page). The precipitate of manganese oxide is titrated with potassium iodide and sodium thiosulphate in the presence of hydrochloric acid. In this method the solubility of ammonium manganese phosphate in the reagents is a very weak point. The ammonium citrate particularly has considerable solvent effect. In order to overcome this difficulty, the solubility of the salt in the reagents was determined. The same amounts of solutions are taken in every analysis and the correction factor for solubility applied to the result obtained. A factor for the solubility of a precipitate is always to be avoided if possible and in this case a great many precautions must be strictly observed to obtain accurate results.

These investigators attempted at first to precipitate the trimanganophosphate in an amorphous state, keeping the excess of manganese in solution with ammonium chloride. They, however, tried to determine the excess of manganese in the filtrate rather than the amount in the precipitate. They evidently attribute the lack of conformity in their results to the oxidation of the manganese before it passes the filter. They discarded the method. The investigations of this thesis were well under way when this paper was found, consequently several of the same experiments were tried. These experiments are discussed in the following paragraphs.

In the precipitation of the trimanganophosphate several difficulties are met with. In the first place, the colloidal precipitate which is first formed is very hard to wash,

and could hardly be considered in a short method on this account. A crystalline precipitate was much to be desired. Braun and Joly mention the two conditions of precipitation of this phosphate and say that the crystalline precipitate is produced on short boiling. This latter salt was the one which was determined upon as the most suitable compound for our purpose. Several qualitative experiments were necessary in order to determine the best way to obtain this precipitate. For this purpose a solution of phosphoric acid was made by dissolving Calcium phosphate in hydrochloric acid and diluting this to a liter. The calcium salt was used in order to more nearly approximate the conditions ordinarily met with in analysis. This solution was standardized (see page) and was used in qualitative as well as quantitative work. It was labeled solution #1. The pro-

cedure finally decided upon for the precipitation is as follows: An excess of manganous chloride is added to the phosphate solution while it is still acid. Ammonia is then added until a white, gelatinous precipitate begins to form. The mixture is then heated until the precipitate has assumed a crystalline form. This requires three or four minutes. Ammonia is again added to alkaline reaction, care being taken not to add any excess as that would precipitate some of the manganese as hydroxide. The liquid is then boiled for three or four minutes, which converts the precipitate into a crystalline form that may be filtered and washed with great ease. Several experiments were made to determine the best indicator for the end of the neutralization. Litmus and rosolic acid were found to be the best for the purpose and preference was finally given to the

latter as it can be used in the solution and gives a more distinct end reaction than the litmus. All of the following experiments were conducted with the use of this indicator. It was prepared according to Sutton. The next point to be determined was just how much this salt consisted of manganese phosphate and nothing else and how complete the precipitation of phosphoric acid could be under these conditions. Contaminations to be expected in this case would be, calcium from the phosphate solution, and manganese by the accidental precipitation of hydroxide due to the addition of an excess of ammonia. Qualitative tests for calcium were made on the precipitate, none of these gave any result. Tests were made on the filtrate from the precipitation for phosphoric acid by the molybdate method. None could be found. It was hereby established that the precipitation of phosphoric

is complete and that no calcium is retained in the precipitate. No tests were made on the precipitate for manganese hydroxide, but that was reserved for later quantitative tests on the effect of ammonium chloride in the solution. Some gravimetric experiments were next carried out, The precipitate was ignited ~~and~~ weighed. This was done to see how closely the precipitate corresponded to the trimanganese phosphate. If this salt had been precipitated it would not change its composition on burning with the exception of some water. If however some ammonium manganese phosphate, or secondary manganese phosphate has been formed, it would burn to the manganese pyrophosphate. 25 c.c. of the calcium phosphate was taken. 5 c.c. of a 15% solution of manganous Chloride was added then ammonia until a slight precipitate was formed. (In all of these

additions of ammonia, the reagent was diluted five or six times, in order to be less in danger of running beyond the end reaction. The mixture was then heated as described above in the qualitative work, until the salt assumes a crystalline form. Then ammonia is added to neutralization and the liquid again boiled. When the precipitate was all crystalline, it was filtered and washed with hot water. The precipitate was then ignited and weighed. The results are given as determinations #1, 2 & 3 in Table 1 on page 30. They do not come up to the calculation for the amount of trimanganous phosphate which should be precipitated from 25 c.c. of the phosphate solution. This amount is given in the standardization. This standardization by the way was by the citrate method. To get some idea of the constitution of this ignited manganese phosphate precipitate, it was redissolved in hydrochloric acid. The

Table #1. Solution #1.

Exp.	Ignited Precipitate	Converted to $Mn_2P_2O_7$	Theoretical $Mn_2P_2O_7$ if ppt. were $Mn_3(PO_4)_2$	NH_4Cl (10%)	
1.	.1475				
2.	.1518	.1809	.1821		
3.	.1541	.1846	.1849		
4.	.1529				
5.	.1540				
6.	.1519				
7.	.1506				
8.	.1520			5 c.c.	
9.	.1544			5 c.c.	
10.	.1554			10 c.c.	
11.	.1543			10 c.c.	
12.	.1546			15 c.c.	
13.	.1517			15 c.c.	

Standardization of Solution #1.

	$Mg_2P_2O_7$	Average P_2O_5	Equals in $Mn_3(PO_4)_2$		
1.	.0992				
2	.0990	.0632	.15812		
3	.0992				
4	.0993				

manganese was then precipitated by boiling with sodium peroxide. This precipitate was dissolved in Hydrochloric acid, with the aid of a little sodium peroxide, and the manganese pre-

cipitated by the addition of an excess of sodium phosphate. The resulting manganese pyrophosphate is given in column 3 of the table. In column 4 is given the amount of pyrophosphate which should have been formed from the weight of the precipitate given in column 2 if it was of the formula $Mn_3(PO_4)_2$. These results tend to show that such of the precipitate as was contained in the ignited product was of this formula. As for the fact that the weight of the phosphate does not come up to the amount of tribasic phosphate calculated for 25 c.c. of the phosphate solution, some of the precipitate may have washed through the filter without having been noticed. Some of the salt may have been redissolved in the washing or the precipitation may not have been complete. As was given above, the molybdate test gave no result with the filtrate when the process was run qualitatively. The conditions may have been

a trifle different in the gravimetric determination, although they were supposed to be the same.

Further precipitations were run in the same way as the above and these results are given as nos. 4, 5 6 and 7 in Table 1 page 30. These results do not show any constant figure. The cause for this seems to have been the imperfect neutralization of the solution with ammonia. This brings up another difficulty. It is absolutely necessary to have an excess of manganese salt in the solution in order to ensure the complete precipitation of the phosphoric acid. On adding ammonia to the solution, the manganese phosphate immediately comes down, as has been seen, but as soon as all of the phosphoric acid is out of solution, manganese commences to precipitate in the form of hydroxide. It is at this point that the addition must be stopped. In anticipation of the

formation of the manganous hydroxide. probably not enough ammonia was added in these cases. To have an excess of the alkali in the solution and still have the manganese salt remain dissolved was the next problem. The requirement is, of course, that not only must the manganous salt remain dissolved, but none of the phosphat precipitate must be taken into solution. Ammonium chloride seemed to be the substance sought for. A 10% solution was made and added in varying quantities to the solution before precipitation. 5 c.c., 10 c.c and 15 c.c. were experimented with. The ammonia was then added until it gave a deep red color with the rosolic acid. The results are given in nos. 8-13 of Table #1, page . Nos. 8 and 9 had 5 c.c. added, nos. 10 and 11 had 10 c.c. and nos. 12 and 13, 15 c.c. Although the results were not very encouraging it was decided that 10 c.c. of the ammonium

chloride had a beneficial effect in preventing the precipitation of the manganese. Comey refers to Brett as authority for the statement that the trimanganous-phosphate is slightly soluble in cold ammonium chloride and nitrate. I have been unable to find the original reference but the above results seem to show that this solubility is not appreciable enough to affect the determination as the higher results are obtained with the salt in the solution. It may be well to state here that this amount of chloride will not prevent the formation of manganic hydroxide if too great an excess of ammonia is added or if the boiling is too long continued in this excess of ammonia.

For the continuation of the experiments it was found necessary to prepare another solution of calcium phosphate, solution "n". This was standardized by both citrate and molybdate methods. The latter

give the only reliable results. The results obtained with this solution are given in Table #2 page 36. The standardization is given in Table #3 on the following page. Two determinations #1 and #2 were made as to the weight of the manganese phosphate obtained from this solution. The results coincide fairly well with each other but not with the amount calculated from the standardization. Four more determinations were made testing the effect of the continuance of boiling after the final addition of ammonia in the precipitation. The resulting weights are given in nos. 3, 4, 5 and 6. No. 3 was just brought to a boil after the final addition of the ammonia. The result was a gelatinous precipitate which filtered and washed very slowly. No. 4 boiled for 3 minutes. It was in the best of condition for washing. No. 5 boiled 6 minutes and no. 6, 10 minutes. The last two were both in fair shape for washing. The conclusions were that boil-

Table #2. Solution #2.

Exper.	Ignited Precipitate	NH_4Cl	NH_4NO_3	$(NH_4)_2SO_4$	K_2SO_4 (10%)	
1.	.1116	10 c.c.				
2	.1121	10 c.c.				
3	.1109	10 c.c.				Brought to a boil
4	.1110	10 c.c.				Boiled 3 minutes
5	.1111	10 c.c.				Boiled 6 minutes
6	.1107	10 c.c.				Boiled 10 minutes
7	.1131	10 c.c.	10 gms.			
8	.1141	10 c.c.	10 gms.			
9	.1117	none	10 gms.			
10	.1118	none	10 gms.			
11	.1121	10 c.c.		10 gms.		
12	.1097	10 c.c.		10 gms.		
13	.1056	none		10 gms.		
14	.1114	none		10 gms.		
15	.1293	10 c.c.			5 c.c.	
16	.1295	10 c.c.			5 c.c.	
17	.1122	10 cc 1st 5 cc. 2nd				Reprecipitated by dissolving in HCl, adding
18	.1102	10 cc 1st 5 cc. 2nd				1 cc. $MnCl_2$ and 5 cc. NH_4Cl
19	.1069	10 cc. 1st 5 cc. 2nd				on second precipitation.
20	.1078	10 c.c.				Reprecipitated by adding
21	.1050	10 c.c.				NH_4OH to HCl solution.
22	$Mn_2P_2O_7$ .1370	10 c.c.	Corresponds to .1141		$Mn_3(PO_4)_2$	Precipitated by adding
23	.1522	10 c.c.	"	.1268	$Mn_3(PO_4)_2$	excess of phosphate to HCl sol.

Table #3. Standardization Solution #2.

	Molybdate method $Mg_2P_2O_7$	Average	$Mn_3(PO_4)_2$		Citrate method $Mg_2P_2O_7$	Average	$Mn_3(PO_4)_2$
1	.0740			1	.0723		
2	.0743	.07417	.1182	2	.0721	.0721	.1149
3	.0741			3	.0719		
4	.0743						

ing had no particular effect as regards the constitution of the precipitate when within reasonably short limits; Also that 4 to 5 minutes was enough to put the precipitate in a good condition to wash. These results also show that if the conditions of precipitation are kept rigidly uniform a uniform precipitate can be obtained.

The effect of such salts as ammonium nitrate and sulphate was next determined. 10 gms. of the salt was used in each case Nos. 7, 8, 9, and 10 were with ammonium nitrate; nos. 11, 12, 13 and 14 with the sulphate. In 7, 8, 11 and 12 the salts were added to the solution along with the customary 10 cc. of ammonium chloride. In 9, 10, 13 and 14 the salts alone were used. These results seem to indicate that

the nitrate has no particular solvent effect, while the sulphate gives variable results. Those in which the nitrate alone was used agree very well with the precipitation in which the chloride alone was used.

Re precipitations were made to see if in this way the effect of the reagents used on the precipitate could be determined and to find out if possible why the weight does not come up to the theoretical. A precipitation was made in the regular way (5 c.c. $Mn Cl_2$ (15%) and 10 c.c. NH_4Cl); the precipitate washed carefully and redissolved in a small quantity of hydrochloric acid. To this 5 c.c. NH_4Cl and 1 c.c. $Mn Cl_2$ were added and the precipitation again made. Nos. 17, 18 and 19 were obtained in this way. 19 boiled longer than the others, and the red color of the rosolic acid had disappeared when the filtration was made. Some ammonium-manganese phosphate had probably been formed. This would account for the

too low result. The others are practically the same as those obtained in the first precipitation. This furnishes additional proof as to the insolubility of the precipitate in ammonium chloride but throws no light on the cause of the low results. Another reprecipitation was made by the addition of ammonia to the hydrochloric acid solution of the first precipitate. The results are given in nos. 20 and 21. These results being so low, it was inferred that some of the trimanganese phosphate was converted into ammonium manganese phosphate. The slight amount of manganese liberated by this reaction would easily have been held in solution by the ammonium chloride formed in the neutralization of the hydrochloric acid. Two of the precipitates of tribasic salt were dissolved up and an excess of phosphate added. The manganese was thus determined as the pyrophosphate. The result is

given in nos. 22 and 23. The weight of trimangano-phosphate as calculated from the amount of manganese in the pyrophosphate, falls within the limits of the weights found gravimetrically in the case of #22 but #23 evidently contained considerable of the manganese chloride which was not removed by washing in the first precipitation. It seems, judging from #22, that part of the precipitate and by far the greater part, is the trimanganous-salt.

Incidentally the behavior of the manganese precipitate in the presence of iron and aluminium salts was tried. 5 c.c. of a 10% solution of alum was added to the phosphate solution when precipitating. The results obtained are given as nos. 15 and 16 in Table #2. These results show that the aluminum takes precedence over the manganese in the formation of the phosphate, and hence that the method is inapplicable in the presence of

aluminum. The experiments with iron were conducted qualitatively. A few drops of iron chloride solution were added to the solution and the precipitation made. No trace iron could be found in the filtrate both with sulphocyanate but the precipitate gave a strong test. That the iron came down as phosphate and not as hydroxide was further evidenced by the form in which the precipitate was found. From these experiments the fact is established that the method cannot be used in the presence of either iron or aluminum salts.

From these results it was concluded that while the precipitate of manganese phosphate as usually obtained is fairly constant if the precautions are rigidly adhered to, it cannot be relied upon as a slight variation will change the composition. The precipitate is too liable to be contaminated with manganese

hydroxide or the ammonium-manganese phosphate. The precipitate in no case corresponds with the tribasic phosphate in composition.

While these results do not promise much in the line of a method for the determination of phosphoric acid, they establish the fact that this precipitation may be used in the separation of phosphoric acid in cases where its removal is desired, of course excepting in the presence of iron and aluminum. An application of this separation is to be found in water analysis. Previous to the analysis of the alkalis the magnesium may be removed by means of phosphoric acid. The manganese salt may be used in removing the excess of phosphoric acid, and the excess of manganese be in turn removed by the use of hydrogen peroxide and ammonia. There is one point however, that needs further elucidation, which was neglected in this work

owing to the limitations of time. Berthelot makes the statement that if this precipitation of manganese phosphate is made in the presence of an alkaline chloride, a double salt will be formed containing two equivalents of manganese to one of the alkali metal. This salt requires some time for its formation and whether or not any of it is formed under the conditions met with in the water analysis. If any of the alkali comes down in the phosphate, the method of separation is of course valueless for this purpose.

The estimation of manganese by the hydrogen peroxide precipitation is not new. In 1877, L. Rosenthal[29] proposed a method for the determination of iron by weighing the precipitate obtained by the peroxide method. His method was to add the peroxide to the acetic acid solution obtained from the precipitation of the iron. The liquid

was then boiled for half an hour to an hour. Ammonia was added until the liquid was neutralized and the solution boiled again until the peroxide was destroyed. Care was taken to add ammonia frequently in small portions in order to keep the liquid slightly ammoniacal. He claimed that the precipitate was Mn_3O_4, except in cases where zinc, barium or other alkaline earth metals were present. In the latter case these metals came down with the precipitate.

In 1880, Wright and Menke[30] made an extensive study of the manganese oxides obtained by various precipitation methods. Eleven methods of preparation of the so called hydrated dioxide were investigated, the method by hydrogen peroxide not being included. However, several general principles were deduced by them which may be of use in the case of the peroxide.

They found that the hydrated dioxide when prepared in the presence of potassium salts always carries down some of the alkali in combination; the amount varying with the conditions. If boiled with potassium hydroxide in the solution the amount of alkali becomes a maximum. The formula in this case becomes $5\,MnO_2 . K_2O$, as previously described by Gorgen. When the precipitation takes place under such conditions that not much potash, or other metallic oxide, can be carried down, a greater or less deficiency in oxygen compared with the manganese dioxide is noticeable. This seems to be due to the fact that some of the manganese is carried down as MnO in place of the K_2O of the above formula. In other words the formula for the precipitate is $5\,MnO_2 . MnO$ under the most favorable conditions. Heating the precipitate appears to diminish the deficiency of oxygen in the

precipitate, that is the tendency is toward the dioxide.

Ad. Carnot[37] (1889) was the first to use the hydrogen peroxide method volumetrically. His procedure is to pour a few c.c. of the peroxide into the cold solution and then to make strongly alkaline with ammonia. The liquid is now boiled for ten minutes to free it from the excess of peroxide. The precipitate is then titrated with oxalic acid and permanganate. In Carnot's first[37] statement of the method he claimed the precipitate to be MnO_2, but later he made a correction[33] and gave the formula as $3MnO_2.MnO$.

Jannasch and Mac Gregory have made a number of investigations on the use of peroxide in the determination of several of the metals, among these being manganese. Their work has been done since Carnot's was published. This method is to add an excess of am-

monium chloride to keep the manganese hydroxide in solution and then to make the solution strongly ammoniacal. Hydrogen peroxide is now added and the mixture boiled to complete the precipitation of the manganese oxide.

The work of Lindeman and Motten[28] (1895), previously mentioned in connection with the manganese phosphate precipitation, was not original so far as concerns their manganese determination, but they incorporate a full account of their method in their article, so reference will be made to it. They precipitate by adding 1-4 cc. of the peroxide to the solution and then making strongly alkaline with 20 c.c. of caustic potash solution while the liquid is still cold. It is then boiled for 10 minutes to free it from the excess of peroxide. The precipitate comes down as a brownish mass which becomes darker and more flocculent

on boiling and separates out rapidly leaving a clear supernatant solution. These investigators claim that this precipitate has the composition 5 Mn_2O_3. MnO. After the peroxide is boiled off the liquid is cooled and 20 c.c. of 20% hydrochloric acid added. This mixture is allowed to stand for a short time, as they say, "to destroy every trace of alkaline peroxide. 20 c.c. of 10% potassium iodide solution is then added and the liberated iodine immediately titrated with thiosulphate solution. The ratio of oxygen to manganese is given as 5 to 6. A point that may be questioned here is their statement that the hydrochloric acid is allowed to stand with the liquid in order to destroy any alkaline peroxide that is left. If any alkaline peroxide were present it would act as a reducing agent in the acid medium and the result would be that some of the manganese precipitate would be

decomposed and the results would come low. Probably no alkaline peroxide is formed in this case. If it is, a source of error is established. Their formula of $5\ MnO_2.MnO$ is not in accordance with the work of Wright and Munke who determine the fact that if caustic alkali is in excess the oxide will go to $5\ MnO_2.K_2O$.

The work done on the manganese determination in this thesis was at the outset merely a few tests to determine the best method for use in connection with the phosphate precipitation. Several obstacles were noted, however, and it was deemed necessary to make several experiments on the peroxide precipitation. In the first trials MnO_2 was used. The manganese solution first used was a standard permanganate solution containing .001118 Mn per c.c. 100 c.c. of this was taken, acidified with hydrochloric acid, and a little sodium peroxide added to

reduce the solution. The liquid was then heated to boiling and sodium peroxide added until the solution was quite alkaline. It was again boiled until the precipitate settled out well. The oxide obtained in this manner was variable in color, ranging from brownish to almost black. The darkest precipitate seemed to have the highest state of oxidation. The precipitate was washed on an ordinary filter, and 25 c.c. of ammonium sulphocyanate solution was added. It was then acidified with dilute sulphuric acid and when the precipitate had dissolved, was titrated with permanganate. The solution must be warmed before titration. The reactions taking place are as follows:- if the oxide formed is $5MnO_2.Na_2O$, the reaction with the sulphocyanate will be the same as though there were the dioxide, MnO_2.

$4MnO_2 + NH_4CNS + 4H_2SO_4 = 4MnSO_4 + (NH_4)_2SO_4 + CO_2 + 2H_2O$.

In this case the ratio of manganese

to sulphocyanate is as 4 to 1, and of manganese to oxygen liberated, as 1 to 1. If the precipitate is $3MnO_2.MnO$ the reaction is:-

$$4(3MnO_2.MnO) + 5NH_4CNS + 24H_2SO_4 = 24MnSO_4 + 5(NH_4)_2SO_4 + 5CO_2 + 14H_2O.$$

In this the ratio of manganese to sulphocyanate is as 24 to 5, while the ratio of manganese to oxygen liberated is 6 to 5. The reaction between the permanganate and sulphocyanate is:-

$$10NH_4CNS + 6K_2Mn_2O_8 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10NH_4CN + 8H_2O$$

The results of the above titrations are given in Table #4 page 52. In #3, the solution was filtered through asbestos and the asbestos washed into the beaker with the precipitate before making the titration. Two more precipitations were made with Na_2O_2, the asbestos filtration also being used. The results from these are given in nos. 4 and 5 of Table #4. The oxide in #4 was blackish while that in #5 was brown in color. The difference in the amount of oxygen

Table #4

100 c.c. $KMnO_4$ contains .1118 Mn. — 10 c.c. NH_4CNS = 11.2 m. $KMnO_4$

Exp.	Precipitant used	NH_4CNS taken	c.c. $KMnO_4$ used up	= NH_4CNS used up	Mn calculated from MnO_2	Mn calculated from $5MnO_2.2MnO$
1	MnO_2	25	5.0	20.5	.05562	.10274
2	MnO_2	25	2.0	23.2	.09690	.11627
3	MnO_2	25	6.8	19.37	.08090	.09708
4	MnO_2	50	29.4	23.75	.09920	.11903
5	MnO_2	50	38.8	15.36	.06416	.07695
6	H_2O_2 - NH_4OH	50	38.4	15.7	.06528	.07868
7	H_2O_2 - NH_4OH	60	54.8	11.07	.04624	.05548

contained may be seen from the calculations to manganese. The black precipitate contains much more oxygen. From these results it was decided that nothing reliable could be obtained by the use of sodium peroxide under these conditions at least. The use of hydrogen peroxide was next considered. Carnot's method was followed out. After several qualitative precipitations in this way in which oxides of various colors ranging from brownish to blackish brown were obtained, some quantitative work was done. #6 and #7 in Table #4 give the

results of the first work. In #6 the solution of manganese was boiled first, the hydrogen peroxide was added to this solution, and then ammonia to strong alkalinity. A blackish brown precipitate that settled well was the result. In #7 the reagents were added to the cold solution and it was then brought to a boil. The resulting precipitate was brownish in color and did not settle out well. The solution was boiled for 15 minutes in each case and the sulphocyanate added directly to the liquid containing the precipitate. These results seemed to indicate that the use of ammonia with the peroxide does not give a uniform compound. To establish this point if possible, the following experiments were carried out.

A standard solution of manganese was first prepared. Manganese carbonate was dissolved in dilute sulphuric acid. Sodium sulphite was added to reduce the solution and the excess

of SO_2 removed by boiling. The solution was standardized by precipitating as $Mn NH_4PO_4$. The standardization is given below.

	Weight $Mn_2P_2O_7$		Weight $Mn_2P_2O_7$
1	.1516	4	.1516
2	.1522	5	.1518
3	.1517	6	.1516

Average .1516 $Mn_2P_2O_7$ = .05875 Mn

25 cc. of the above solution was taken for each determination. The solution was heated to boiling, 5 cc. H_2O_2 added, then a large excess of NH_4OH and the mixture boiled again. The results are given in Table #5, page 56. No. 1 was boiled 10 minutes, #2, 15 minutes and #3, 20 minutes. Taking these results into consideration the other determinations were boiled 15 minutes. 30 cc. of NH_4CNS was added to the hot liquid and the titration completed as usual. It will be seen that #7, 8 and #12 agree fairly well with the amount that should be found, when the mangan-

ere is calculated from the formula MnO_2 or $5\ MnO_2 . (NH_4)_2O$. The others seem to show a higher state of oxidation. One thing that is very evident from these precipitations is that the composition is not uniform under these conditions.

Thinking that possibly the sulphocyanate titration might be responsible for these variations, a standard solution of oxalic acid was made and used in place of it. The oxalic acid was made up so that 1 c.c. equaled 1 c.c. permanganate. The results of the titrations are given in Table #6. In #1 and #2 the solution was heated to boiling and 5 c.c. each of H_2O_2 and NH_4OH was added. After boiling for a little time, the precipitate was filtered out, washed and titrated with the oxalic acid. In #3 and #4 the H_2O_2 was added to the boiling solution and then dilute ammonia added very slowly as Rosenthal recommended. The state of oxidation in these seems to have been

Table #5

30 c.c. NH_4CNS = 34.8 c.c. $KMnO_4$ — 25 c.c. Mn sol. = .05875

Exp.	c.c. NH_4CNS	c.c. $KMnO_4$ need	= NH_4CNS used up	Mn calculated from MnO_2	Mn calculated from $5MnO_2 \cdot MnO$	
1	30	17.75	14.7	.06140	.07367	
2	30	17.3	15.09	.06303	.07563	
3	30	17.3	15.09	.06303	.07563	
4	30	17.3	15.09	.06303	.07563	
5	30	18.0	14.48	.06048	.07257	
6	30	17.5	14.91	.06227	.07472	
7	30	18.4	14.14	.05906	.07086	
8	30	18.2	14.31	.05977	.07172	
9	30	18.1	14.4	.06014	.07217	
10	30	17.4	15.0	.06265	.07518	
11	30	18.0	14.48	.06048	.07257	
12	30	18.7	13.88	.05797	.06956	

lower than in any of the other experiments. In #5 and #6 the dilute ammonia was added directly after the peroxide. In these cases the titration is made without filtration of the oxide. In #7 and #8, 10 c.c. H_2O_2 was used, added to the boiling solution, and 5 c.c. strong ammonia directly afterwards. The precipitate was filtered and washed. In #9, 10 and 11. H_2O_2 was added

Table #6.

25 cc. $H_2C_2O_4$ = 25 cc. $KMnO_4$ =

Exp.	c.c. $H_2C_2O_4$	c.c. $KMnO_4$ used	c.c. $H_2C_2O_4$ used up	mm Calculated from MnO_2	mm Calculated from $5MnO_2.MnO$
1	25	11.7	13.3	.03395	.04074
2	25	11.6	13.4	.03420	.04104
3	25	14.9	10.1	.02578	.03369
4	25	20.3	9.7	.02477	.02971
5	25	13.7	11.3	.02884	.03461
6	25	13.7	11.3	.02884	.03461
7	25	11.1	13.9	.03548	.04257
8	25	12.2	12.8	.03267	.03921
9	25	6.5	18.5	.04722	.05666
10	25	6.7	18.3	.04671	.05605
11	25	6.8	18.2	.04645	.05574

in the cold and 15 cc. NH_4OH immediately afterward. The excess of peroxide was boiled off. These last three give results nearer those calculated for the formula $5MnO_2.MnO$ than any other of the tests, but even these are two or three milligrams off. Considering the results obtained in all these titrations, there does not seem to be much room for considering the formula of the precipitate

Table #7

1-4 } 10 cc. NH_4OH = 11.7 cc. $KMnO_4$ — 5-7 } 10 cc. NH_4OH = 11.5 cc. $KMnO_4$

Exp.	cc. NH_4OH	cc. $KMnO_4$ used	cc. NH_4OH used up	Mn calculated from Mn_2O_3	Mn calculated from $5Mn_2O_3 \cdot MnO$
1	25	11.05	15.55	.06495	.07793
2	25	11.1	15.5	.06474	.07768
3	25	11.0	15.6	.06516	.07818
4	25	11.1	15.5	.06474	.07768
5	25	10.7	15.65	.06537	.07843
6	25	10.75	15.6	.06516	.07818
7	25	10.65	15.7	.06557	.07868

obtained as $5Mn_2O_3 \cdot MnO$. These results come nearer the formula Mn_2O_3, although the titrations with oxalic acid do not. The precipitations in which the oxalic acid was used if we except the last three, were made according to modes of procedure which are not generally used in the analysis by this method. Judging from the number of determinations made and the different variations tried, we are safe in saying that the oxide obtained with the use of NH_4OH is not of a uniform composition; its state of oxidation varies with

slight changes in the conditions.
The process of Lindeman and Notten was next tried. Caustic soda was used instead of caustic potash and instead of the iodometric method of titration, sulphocyanate was used. 10 cc. of H_2O_2 was added to the manganese solution in the cold, then 20 cc. of a 10% caustic soda solution. The liquid was then boiled for fifteen minutes to free it from peroxide. The titration was carried out as usual. The results are given as #1, 2, 3 and 4 of Table #7 page . Nos. 5, 6 and 7 of the same table are determinations made two or three weeks later with a different permanganate solution. In these latter 5 cc. H_2O_2 and 25 cc. NaOH solution were used, otherwise the conditions were the same. The results are certainly uniform and close enough for most work. They do not give for the formula of the precipitate, however, any such formula as proposed by Lindeman and Notten, ($5MnO_2 \cdot NaO$).

Nor do they give the proportions which Wright and Menke have stated for such conditions, ($5 Mn_2O_7 . Na_2O$). This latter formula, however, seems to more nearly approach the truth. It is in reality a manganite, $Na_2Mn_5O_{11}$. The results given in Table #7 seem to show that the precipitate is in reality of a higher state of oxidation even than this manganite, and that the precipitate lies somewhere between this manganite and a manganate. Calculating from the amount of oxygen liberated and the amount of manganese known to be present, (the ratio of oxygen liberated is to manganese as 11 to 10) - a salt with a formula something like $Na_2Mn_{10}O_{22}$ or $Na_4Mn_{10}O_{23}$ is obtained. It may be that some sodium manganate is carried down by the precipitate so that it forms these proportions. This would give $9 Mn_2O_7 . Na_2Mn_2O_4$, Such however is merely conjecture.

In summing up the results

of the study of the manganese precipitation it has been found:-

(1) That the precipitation by Na_2O_2 is not expedient nor accurate, owing to the length of time required and the difficulty in washing the precipitate free from Na_2O_2.

(2) That the precipitation by the use of H_2O_2 and ammonia does not yield uniform results, the state of oxidation seeming to vary with the slightest change of condition in the precipitation.

(3) That a constant precipitate may be obtained by using hydrogen peroxide and caustic alkali, but that this precipitate is not of the composition attributed to it by several authors. It is of a higher oxidation.

In conclusion, the method of phosphate analysis aimed at in this thesis has not proven practicable. This is due to two facts,- the difficulty of obtaining the trimanganophosphate in a pure state free

from contamination, and the question in regard to the composition of the manganese oxide precipitated by peroxide. While the real aim has not been attained, several interesting facts have been brought forth by these investigations. The possibility of the separation of phosphoric acid by means of manganese salts has been proven. Secondly, the evidence which points to the precipitate of manganese oxide as belonging to a higher state of oxidation than is usually conceded. More work must be done on both of these subjects before they can be settled definitely.

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